Inorganica Chimica Acta, 48 (1981) 1–7
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The Aquation and *Trans*-Influence of Phosphites in Complexes of Ruthenium(II)

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Received October 2, 1980

The complexes trans-*[*$Ru(NH_3)_4(P(OR)_3)_2$*]*$^{2+}$ *and* trans-*[*$Ru(NH_3)_4P(OEt)_3P(OR)_3$]$^{2+}$, *where R = methyl, isopropyl and butyl, aquate* via *a common mechanism to yield, in each system, a single monophosphite complex as the product. The rate constants range from* 9.2×10^{-5} sec^{-1} *(OEt–Ru–O*^{i}*Pr) to* 1.2×10^{-5} sec^{-1} *(OMe–Ru–OMe), (25 °C,* $\mu = 0.10$, $C_{H^+} = 10^{-1}$–10^{-4} M*). With the complexes containing two different phosphorus ligands, the aquation generates only the most stable monophosphite complex.*

The formal reduction potentials for tetraammineruthenium (III)–(II) couples with trimethyl, tributyl, and triisopropyl phosphite as ligands are +0.74, +0.67 and +0.66 V, respectively (25 °C, $\mu = 0.10$, $C_{H^+} = 10^{-1}$–10^{-4} M*). The complexes* trans-*[*$Ru(NH_3)_4P(OR)_3(H_2O)$*]*$^+$ *exhibit an absorption band at 316 nm (*$\epsilon < 8 \times 10^2$ M^{-1} *cm*$^{-1}$*) attributed to d–d transitions and the derivatives* trans-*[*$Ru(NH_3)_4P(OR)_3pz$*]*$^{2+}$ *present ligand-to-metal charge-transfer bands near 366 nm, respectively, (*$\epsilon > 3 \times 10^3$ M^{-1} *cm*$^{-1}$*). The association constants for the complexes* trans-*[*$Ru(NH_3)_4P(OR)_3pz$*]*$^{2+}$*, measured spectrophotometrically, increase according to the following sequence:* $P(OMe)_3 < P(OEt)_3 < P(OBut)_3 < P(O^iPr)_3$*. The formal potentials for the Ru(III)/Ru(II) couples of the monophosphite complexes studied and the formation constants for the derivatives* trans-*[*$Ru(NH_3)_4P(OR)_3pz$*]*$^{2+}$ *strongly suggest the relevance of the* d_π *electrons in the ruthenium (II)–phosphite bond. The extention of Ru(II)* → *P(III) back-bonding for these phosphite complexes decrease as follow:* $P(OMe)_3 > P(OEt)_3 > P(OBut)_3 > P(O^iPr)_3$*.*

Introduction

The chemistry of complexes containing phosphorus ligands is an exceedingly rich area for exploration, both with respect to changes in the chemical properties of the coordinated phosphorus ligand and variations in the reactivity of the metal center [1–6].

In view of their unique properties [7–9], the ruthenium (II) and (III) ammine complexes were chosen as the starting point for systematic studies having as their goal an understanding of the basic chemistry of phosphites as ligands in normal octahedral environments. To avoid additional complications, our initial studies have focused on small ligands with a single coordination site. Binuclear complexes bridged by polyphosphite ligands are currently being investigated in our Laboratory.

We have previously reported general synthetic routes [6] for the preparation of *trans*-[$Ru(NH_3)_4P(OR_1)_3P(OR_2)_3$]$X_2$, ($R_1 = R_2$, $R_1 \neq R_2$; X = PF_6^- or $CF_3SO_3^-$), the synthesis of *trans*-[$Ru(NH_3)_4P(OEt)_3(H_2O)$]X_2, and kinetic studies of ligand [5] substitution for the *trans*-[$Ru(NH_3)_4P(OEt)_3(H_2O)$]$^{2+}$ complex ion.

The present work reports kinetic data for the aquation of *trans*-[$Ru(NH_3)_4P(OR_1)_3P(OR_2)_3$]$^{2+}$ ($R_1 = R_2$, $R_1 \neq R_2$) complex ions, as well as other data which permit an evaluation of the *trans*-influence of phosphites.

Experimental

Chemical and Reagents

The solvents employed were freshly distilled before use. The phosphites (Aldrich) were purified by treatment with metallic sodium followed by vacuum distillation [5]. Doubly distilled water was used throughout. Pyrazine, pz, (Aldrich Puriss grade) was used as supplied. All experiments and manipulations were carried out under a purified Ar or N_2 atmosphere using standard procedures [10].

Synthesis of Ruthenium Compounds

The starting material for the synthesis of the ruthenium compounds was pure [$Ru(NH_3)_6$]Cl_3 purchased from Mathey Bishop, Inc.

[$Ru(NH_3)_5Cl$]Cl_2, *trans*-[$Ru(NH_3)_4SO_2Cl$]Cl and *trans*-[$Ru(NH_3)_4SO_2(H_2O)$]Cl_2 were prepared following literature methods [9].

trans-[$Ru(NH_3)_4(P(OR)_3)_2$](CF_3SO_3)$_2$, (where R = methyl, ethyl, isopropyl and butyl). These complexes were synthesized by reacting *trans*-[$Ru(NH_3)_4$-

$SO_2(H_2O)](CF_3SO_3)_2$ with the desired phosphite in acetone under an Ar or N_2 atmosphere [6]. The excess of phosphite and the solvent were eliminated by rotoevaporation. The yellow solids obtained were purified by precipitation from saturated ethanol solution with peroxide-free ether.

trans-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_2$ was obtained *via* aquation [5] of *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2](CF_3SO_3)_2$ in a degassed solution of CF_3SO_3H (10^{-3} *M*). The residue obtained after elimination of the solvent by rotoevaporation was purified by reprecipitation from saturated ethanol solution.

trans-$[Ru(NH_3)_4P(OEt)_3P(OR)_3](CF_3SO_3)_2$, R = methyl, isopropyl and butyl. These complexes were prepared by reacting *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_2$ with the desired phosphite in acetone. The complex was obtained as a solid and purified by reprecipitation as described above.

Detailed procedures for the preparation of the phosphite complexes were described in our former paper [6]. The purity of the complexes was checked by cyclic voltammetric and spectrophotometric measurements.

Apparatus and Techniques

Ultraviolet and visible spectra were recorded on either a Perkin-Elmer model 575 or a Cary model 14 spectrophotometer. The temperature of the cell compartment of the spectrophotometers was maintained constant within ±0.1 °C using a HAAKE thermostat.

Cyclic voltammograms were recorded on a PAR model 170 or an Electroscan 30 unit. The cell employed a S.C.E. as the reference electrode and a carbon paste indicator electrode. The formal potentials were converted to the N.A.E. reference by adding 242 mV. The reversibility of the systems was verified by applying two criteria: a) comparing the ratio of the peak current for the cathodic process relative to that for the anodic process [11], b) comparing the peak-to-peak separation with that of the $Ru(NH_3)_6^{3+/2+}$ system, known to be reversible [12].

Kinetic Measurements

The complexes dealt with in this study are not extremely air sensitive; nonetheless, whenever possible, all-glass connections were employed and routine techniques for transferring air sensitive materials utilized [10]. Care was also taken to avoid exposure of the solutions of the phosphite complexes to light. Solutions with the pH and ionic strength previously adjusted were made up in a Zwickel flask immersed in a constant-temperature bath. After deaeration of these solutions, a weighted amount (10–20 mg) of the solid bisphosphite complex was added quickly to the Zwickel flask connected to a spectrophotometric cell fitted with two stopcocks. After the dissolution of the solid (2–5 min), the solution was transferred by gas pressure into the connected spectrophotometric cell. The rate of the loss of the ligand was measured by following the change in absorbance at 316 nm. The aquation products were characterized by cyclic voltammetric and spectrophotometric measurements. First order rate constants were determined graphically in the usual manner from plots of log $(A_\infty - A_t)$ *versus* time (where A_∞ and A_t are the final absorbance and that at time t, respectively). The plots log $(A_\infty - A_t)$ *versus* time were linear for at least four half-lives.

The activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were evaluated from log k_{-1}/T and $1/T$ data. The data were analysed with a conventional least-squares program employing a HP-97 calculator.

In comparing the relative aquation rates of the series *trans*-$[Ru(NH_3)_4(P(OR)_3)_2]^{2+}$ to those for *trans*-$[Ru(NH_3)_4P(OEt)_3P(OR)_3]$, as well for evaluating the activation parameters the k_{-1} values of the former, (Table II), must be divided by a statistical factor of 2 since they have two identical phosphorus ligands.

Equilibrium Constant Determinations

In a typical experiment, standard solutions of pyrazine (0.800 *M*) were separately degassed in a flask tightly covered with a serum cap and vented through a syringe needle. An aliquot (0.5–1.0 ml) of the ligand solution was transferred using syringes to a Zwickel flask containing 10–30 ml of the degassed *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ solution with ionic strength and pH previously adjusted. Using gas pressure, the spectrophotometric cell was filled and the absorbance measured at the selected wavelength. The agreement among the absorbance data for the same solution obtained 2, 5, 10 and 20 minutes after the mixing of the ligand and monophosphite complex solutions indicates that the equilibrium is established rapidly in such systems.

The absorbance measurements for pyrazine complexes were performed at 366 nm. Since only one species is formed in each case, the equilibrium constants were accessible by measuring the absorbance of the solutions containing the same concentration of the monophosphite complex, C_x, and variable concentrations of the ligand pz. Changing the ligand concentrations from C'_L to C''_L, the concentrations of complex formed will be C'_z and the absorbance values A_1 and A_2 respectively.

Since $C''_z:C'_z = A_2:A_1 = p$, the association constant could be easily calculated from the equations [13]:

$$C'_z = \frac{C_x(C''_L - pC'_L)}{p(C''_L - C'_L))}$$

and

$$K = \frac{pC'_z}{(C_x - pC'_z)C''_L}$$

TABLE I. Band Maxima, Molar Absorptivity[a] and Formal Reduction Potentials[a] for Ruthenium Monophosphite Complexes.

Complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	E$^{o'}$ (V *vs.* N.H.E.)
trans-$[Ru(NH_3)_4P(OMe)_3(H_2O)]^{2+}$	316	$7.3 \pm 0.3 \times 10^2$	$+0.74 \pm 0.01$
trans-$[Ru(NH_3)_4P(OMEt)_3(H_2O)]^{2+}$[b]	316	$6.5 \pm 0.2 \times 10^2$	$+0.70 \pm 0.01$
trans-$[Ru(NH_3)_4P(OBut)_3(H_2O)]^{2+}$	316	$5.4 \pm 0.3 \times 10^2$	$+0.67 \pm 0.02$
trans-$[Ru(NH_3)_4P(O^iPr)(H_2O)]^{2+}$	316	$5.6 \pm 0.3 \times 10^2$	$+0.66 \pm 0.01$

[a] Temp. = 25 ± 0.1 °C; $\mu = 0.10$ $NaCF_3COO$; $C_{H^+} = 1.0 \times 10^{-3}$ M^{-1}. The monophosphite complexes were generated in solution by aquation of the respective bis phosphite complexes. [b] Reference (5).

The *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ complexes were generated in solution *via* aquation of the corresponding *trans*-$[Ru(NH_3)_4(P(OR)_3)_2]^+$ complexes.

Results and Discussion

The biphosphite complex ions present two absorption bands at 292 and 260 nm as expected on the basis of their D_{4h} symmetry [6]. The aquation of these complexes leads to spectral changes since the monophosphite complexes, *trans*-$[Ru(NH_3)_4P(OR_1)_3(H_2O)]^{2+}$, possess C_{4v} symmetry. In this case, the absorption band was attributed to an $A_1^1 \rightarrow E^1$ transition. The spectral characteristics for the monophosphite complexes are listed on Table I. Due to the loss of the center of symmetry, the molar absorptivity of the monophosphite complexes is higher than that of the corresponding bisphosphite complexes [6].

The formal reduction potentials for the monophosphite complexes, (see Table I), were obtained from reversible waves in cyclic voltammetry. The E$^{o'}$ data for the Ru(III)/Ru(II) couples of these complexes follow the same trend observed for the bisphosphite complexes [6]. The formal redox potentials, E$^{o'}$, become more positive as the basicity of the phosphorus ligand decreases.

The effect of increasing the hydrophobicity of the phosphite ligand, which might potentially give rise to more positive E$^{o'}$ values, should be negligible according to literature data [14].

The E$^{o'}$ values in Table I are in accord with this expectation since they follow the order of increasing Ru(II) → P(III) back-bonding strength, *i.e.* increasing π-acceptor ability of the phosphites, in the series: $P(O^iPr)_3 < P(OBut)_3 < P(OEt)_3 < P(OMe)_3$. However, since the Ru(III) center is a good σ acid, the enhancement of the basicity of the phosphorus atom could also stabilize Ru(III) with respect to Ru(II) to the same extent. Both considerations are in agreement with the experimental data. In dealing with biphilic ligands such as phosphites, great care should be taken in the interpretation of E$^{o'}$ differences since both σ and π bonding interactions may be important and very difficult to analyse separately. Nevertheless, an estimate of the σ-donor abilities of phosphites in stabilizing Ru(III) may be obtained by comparing the affinity [5] of $P(OEt)_3$ for *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+}$.

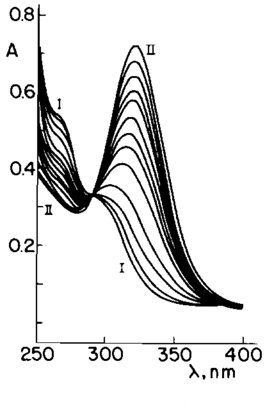

Fig. 1. Changes in electronic spectra associated with the aquation of *trans*-$[Ru(NH_3)_4(P(O^iPr)_3)_2]^{2+}$: I) t = 0; (II) after 70 h; $\mu = 0.10$ ($NaCF_3COO$); $C_{H^+} = 1.0 \times 10^{-3}$; $C_{Ru(II)} = 1.3 \times 10^{-3}$ M.

The equilibrium constant for the reaction:

$$\textit{trans}\text{-}[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+} + P(OEt)_3 \rightleftarrows \textit{trans}\text{-}[Ru(NH_3)_4(P(OEt)_3)_2]^{2+} + H_2O$$

is 3.3×10^4. The formation constant for the corresponding Ru(III) complex is 30. These data strongly suggest that the π-acceptor properties of phosphites should be the most significant effect present and that the E$^{o'}$ shift is due mainly to stabilization of Ru(II) relative to Ru(III). Similar considerations have been applied for trialkylphosphines in mixed phosphine 2,2'-Bipiridine complexes of Ruthenium [15].

The aquation of two series of bisphosphite complexes is investigated in this paper. In one series, identical phosphites are coordinated in the *trans*

TABLE II. Rates of Aquation for *trans*-$[Ru(NH_3)_4(P(OR)_3)_2]^{2+}$ Complexes.

Complex	k_{-1}[a] sec^{-1}	Temp. °C	C_{H^+} *M*	ΔH≠ kcal/mol	ΔS≠ cal/k^0 mol
trans-$[Ru(NH_3)_4(P(OMe)_3)_2]^{2+}$	4.62×10^{-4}	42.6	1.0×10^{-3}	31.0 ± 0.8	22 ± 3
	1.58×10^{-4}	35.6	1.0×10^{-3}		
	1.64×10^{-4}	35.5	1.0×10^{-1}		
	1.58×10^{-4}	35.5	1.0×10^{-2}		
	1.60×10^{-4}	35.5	1.0×10^{-4}		
	6.79×10^{-5}	30.8	1.0×10^{-3}		
	2.41×10^{-5}	25.1	1.0×10^{-3}		
trans-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$	2.2×10^{-5} [b]	25.0	1.0×10^{-3}	28.5 ± 0.5	12 ± 2
trans-$[Ru(NH_3)_4(P(O^iPr)_3)_2]^{2+}$	4.98×10^{-4}	38.6	1.0×10^{-3}	23.0 ± 0.5	−1.8 ± 2
	2.18×10^{-4}	32.1	1.0×10^{-3}		
	2.12×10^{-4}	32.1	1.0×10^{-1}		
	2.17×10^{-4}	32.1	1.0×10^{-4}		
	8.02×10^{-5}	24.2	1.0×10^{-3}		
	4.34×10^{-5}	20.0	1.0×10^{-3}		
trans-$[Ru(NH_3)_4(P(OBut)_3)_2]^{2+}$	7.4×10^{-5} [c]	32.5	1.0×10^{-3}	26.0 ± 1	5.2 ± 3
	3.2×10^{-5} [c]	25.2	1.0×10^{-3}		
	1.9×10^{-5} [c]	25.2	1.0×10^{-3}		
	9.4×10^{-6} [c]	19.4	1.0×10^{-3}		
	2.0×10^{-5} [d]	24.0	1.0×10^{-3}		
	1.9×10^{-5} [c]	24.0	1.0×10^{-3}		
	1.7×10^{-5} [e]	24.0	1.0×10^{-3}		
	1.5×10^{-5} [f]	24.0	1.0×10^{-3}		
	1.9×10^{-5} [c]	25.2	1.0×10^{-2}		
	1.9×10^{-4} [c]	25.2	1.0×10^{-4}		

[a] $\mu = 0.10$, $(NaCF_3/COO/CF_3COOH)$, $C_{Ru(II)} = 5.0 \times 10^{-4}$ *M*. Each value is the mean of at least three independent determinations, which agreed to within ±3%. [b] Reference 5. [c] % Ethanol/water medium: = 50/50; [d] = 80/20; [e] = 30/70; [f] = 10/90.

position to the same Ru(II) center. In the other series, complexes with two different phosphites are considered. All the complex ions *trans*-$[Ru(NH_3)_4P(OR_1)_3P(OR_2)_3]^{2+}$, ($R_1 = R_2$ or $R_1 \neq R_2$), in aqueous acidic media ($C_{H^+} > 10^{-5}$ *M*), invariably generate only one defined monophosphite complex.

These reactions were followed simultaneously by spectrophotometry and cyclic voltammetric measurements. Figures 1 and 2 present typical changes in electronic and polarographic spectra during such reactions.

The kinetic data for the formation of the monophosphite complexes are listed in Tables II and III. The kinetic data obtained in acidic media are in accord with the following rate law:

$$\frac{d\ trans\text{-}[Ru(NH_3)_4P(OR_1)_3(H_2O)]^{2+}}{dt} = k_{-1}\ trans\text{-}[Ru(NH_3)_4P(OR_1)_3P(OR_2)_3]^{2+}$$

where $R_1 = R_2$ or $R_1 \neq R_2$.

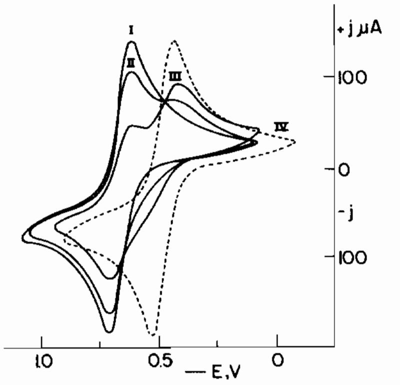

Fig. 2. Changes in polarographic spectra associated with the aquation of *trans*-$[Ru(NH_3)_4(P(OMe)_3)_2]^{2+}$: I) t = 0; II) after 2 h; III) 8 h; IV) 70 h. Carbon paste electrode; scan rate 200 mV/sec; $\mu = 0.10$ $NaCF_3COO$; $C_{H^+} = 1.00 \times 10^{-3}$; $C_{Ru(II)} = 1.0 \times 10^{-3}$ *M*.

TABLE III. Rates of Aquation for *trans*-$[Ru(NH_3)_4P(OEt)_3P(OR)_3]^{2+}$ Complexes.

	k_{-1}[a] sec^{-1}	Temp. °C	C_{H^+} *M*	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ cal/k^0 mol
$P(OMe)_3$	3.50×10^{-4}	41.2	1.0×10^{-3}	30.0 ± 0.8	20 ± 3
	1.05×10^{-4}	34.5	1.0×10^{-3}		
	1.01×10^{-4}	34.5	1.0×10^{-2}		
	1.00×10^{-4}	34.5	1.0×10^{-1}		
	1.04×10^{-4}	34.5	1.0×10^{-4}		
	2.51×10^{-5}	25.6	1.0×10^{-3}		
	1.04×10^{-5}	20.0	1.0×10^{-3}		
$P(O^iPr)_3$	6.42×10^{-4}	40.9	1.0×10^{-3}	21.0 ± 0.5	−7.0 ±2
	2.89×10^{-4}	35.4	1.0×10^{-3}		
	2.82×10^{-4}	35.4	1.0×10^{-1}		
	2.79×10^{-4}	35.4	1.0×10^{-4}		
	1.19×10^{-4}	26.5	1.0×10^{-3}		
	4.73×10^{-5}	20.0	1.0×10^{-3}		
$P(OBut)_3$	3.35×10^{-4}	44.9	1.0×10^{-3}	27.1 ± 1	9.8 ± 3
	7.31×10^{-5}	35.0	1.0×10^{-3}		
	7.27×10^{-5}	35.0	1.0×10^{-1}		
	7.34×10^{-5}	35.0	1.0×10^{-4}		
	4.08×10^{-5}	30.2	1.0×10^{-3}		
	7.71×10^{-6}	20.0	1.0×10^{-3}		

[a] $\mu = 0.10$ ($NaCF_3COO/CF_3COOH$); $C_{Ru(II)} = 1.0 \times 10^{-5}$ *M*. Each entry is a mean of at least three independent determinations, which agreed to within ±3%.

In solutions where $[H^+] < 10^{-5}$ *M*, the reaction rates decrease and in alkaline media decreases of about one order of magnitude can be observed. In alkaline media phosphite solutions are reasonably stable [16, 17]. Thus, under these conditions, the association of $P(OR)_3$ with the monophosphite complexes becomes more significant as the hydrogen ion concentration decreases. This effect is not observed in acidic media where trialkyl-phosphites solutions are quite unstable [16–17]. Based on these observations the following general mechanism is proposed for the aquation of the diphosphite complexes:

$$trans\text{-}[Ru(NH_3)_4(P(OR)_3)_2]^{2+} + H_2O \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}}$$

$$\begin{tikzcd} trans\text{-}[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+} + P(OR)_3 \arrow[d, "\text{fast}"', "+\,H_3O^+"] \\ P(OH)(OR)_2 + ROH \end{tikzcd}$$

In the presence of a competing ligand such as sulphite or imidazol, good agreement is observed between the rate data obtained in alkaline and those measured in acidic media. This provides additional experimental support for the above observation.

In acid medium, k_{-1} is the rate determining step and is in the range of 9.5×10^{-6}–9.2×10^{-5} sec^{-1}, at 25 °C, for all the complexes studied here. Taking in account the similarity of the trialkyl-phosphites employed in this study, k_1 should be similar to the value measured for triethyl phosphite [5], 0.75 sec^{-1} in all cases.

Our present data permit new arguments in favour of the proposed mechanism [5]. It is known [16–18] that the different phosphites hydrolyse at different rates. As pointed out above, only one of two possible products is detected for the reactions with the mixed diphosphite complexes. Thus, it seems unlikely that the leaving group is attacked by a water molecule while still coordinated to the Ru(II) center. Reactions carried out in aqueous-ethanolic media for the *trans*-$[Ru(NH_3)_4P(OBut)_3)_2]^{2+}$ system also corroborate the hypothesis of a dissociative mechanism. Upon changing the composition of the medium from 80% to 10% ethanol, the rates only varied by 25%, the observed rate constants increasing as the water content of the medium decreases.

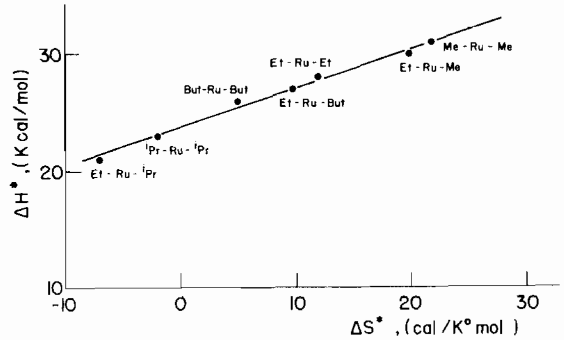

Fig. 3. Plot of $\Delta H^{\neq}$ *vs.* $\Delta S^{\neq}$ for the aquation of *trans*-[Ru$(NH_3)_4P(OR_1)_3P(OR_2)_3]^{2+}$, $R_1 \neq R_2$ and $R_1 = R_2$, complexes.

TABLE IV. Equilibrium Data for the Reaction: *trans*-[Ru$(NH_3)_4LH_2O]^{2+}$ + pz $\rightleftarrows$ *trans*-$[Ru(NH_3)_4Lpz]^{2+}$ + H_2O.

L	K, M^{-1}	Ref.
NH_3	22×10^9	(8)
SO_2	40	(9)
$SO_3^=$	29×10^2	(9)
$P(OMe)_3$[a]	16 ± 1	
$P(OEt)_3$[a]	20 ± 2	(5)
$P(OBut)_3$[a]	24 ± 2	
$P(O^iPr)_3$[a]	31 ± 3	

[a] μ = 0.10 ($NaCF_3COO$; $NaCH_3COO/CH_3COOH$); Temp. = 25.0 ± 0.1 °C; pH = 5.2; $C_{Ru(II)} = 9.2 \times 10^{-5}$ *M*; present work unless otherwise indicated.

Figure 3 presents an isokinetic plot for these reactions. A good confirmity is observed for the seven systems studied, suggesting that all these reactions take place by the same mechanism [19, 20].

The mutual ligand *trans*-influence is another point to be considered here. Comparing the $\Delta H^{\neq}$ parameter for the aquation of the *trans*-$[Ru(NH_3)_4P(OR)_3)_2]^{2+}$ complexes, a trend can be observed. As the π acid strength of the phosphite ligand increases, the energy required to break the Ru(II) → P(III) bond increases.

For the mixed diphosphite complexes, *trans*-[Ru$(NH_3)_4P(OEt)_3P(OR_i)_3]^{2+}$, the final equation complexes were *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ when R_i = $P(O^iPr)_3$ or $P(OBut)_3$ and *trans*-$[Ru(NH_3)_4P(OMe)_3(H_2O)]^{2+}$ when R_i = $P(OMe)_3$. Selectivity is evident, reflecting the competition for the Ru(II) d_π electrons which should exist between the *trans* ligands. Thus, the stronger d_π electron withdrawing group reduces the bonding between the Ru(II) center and the other *trans* phosphorus ligand. The aquation product will be the more stable monophosphite complex in which the stronger Ru(II)–P(III) bond is maintained.

It is important also to point out that, as inferred from E° data, the affinity of phosphites for Ru(II) increases as the steric order decreases [21]: $P(O^iPr)_3 \cong P(OBut)_3 < P(OEt)_3 < P(OMe)_3$. Thus, in the aquation of diphosphite complexes both back-bonding and steric effects will work in the same direction. However, the $P(OR)_3$ ligands dealt with in this paper are simple molecules and as judged from their C.P.K. molecular models the steric effects are not so relevant as back-bonding effects despite their constant participation. An exception to this occurs in triisopropyl case.

Except in the case of the triisopropyl phosphite complex, all the other ligands aquate at comparable rates in both series of complexes. For the *trans*-$[Ru(NH_3)_4(P(OR)_3)_2]^{2+}$ complexes, the $P(O^iPr)_3$ ligand exhibits k_{-1} values about 4 times larger than those of its homologs. The fact that the back-bonding Ru → $P(O^iPr)_3$ should be the weakest in this series of complexes, the unfavorable entropy change, and the existence of some steric hindrance between the two *trans* phosphorus ligands could account for the experimental results. One might expect in principle a faster rate of aquation for the phosphite complexes having two identical ligands (as a result of the statistical factor of 2). It is interesting to note however that the observed aquation rate constants for both series of complexes are essentially the same.

The $\Delta H^{\neq}$ variations for the bond breaking of the same ligand in both series are unfortunately small and within the limit of the experimental error.Since these uncertainties also pertain for the $\Delta S^{\neq}$ data, it is difficult to establish any good correlation.

Although the relevance of the back-bonding in Ru(II) → P(III) complexes has been pointed out on the basis of the E° data and the aquation studies, we felt it best to check this hypothesis experimentally. The pyrazine molecule, a strong π acid and a very weak σ base [22] pK = 0.5, was chosen for this purpose since the participation of the σ and π components in the pyrazine complexes of Ru(II) is well established [23, 24]. Accordingly, the changes in the affinities of the monophosphite complexes for pz, measured by the formation constants of the *trans*-$\{Ru(NH_3)_4P(OR)_3pz]^{2+}$ complexes, may be used for estimating the availability of the d_π electrons of the Ru(II) center and the so-called '*trans*-influence' in such systems [25].

The pyrazine monophosphite derivatives absorb at 366 nm and the molar absorptivities are in the 3.8×10^3–4.8×10^3 M^{-1} cm^{-1} range. These metal-to-ligand charge transfer (MLCT) bands are similar to those described in a former paper [5] for the *trans*-$[Ru(NH_3)_4P(OEt)_3pz]^{2+}$ complex. They are assumed to be $d_{\pi-\pi}{}^*$ transitions and provide a convenient means of monitoring the reactions studied.

Table IV summarizes formation constants and spectral data for Ru(II)–pz derivatives for selected complexes. Enormous changes in affinity of the complex *trans*-$[Ru(NH_3)_4L(H_2O)]^{2+}$ for pz as ligand are observed. The formation constants for the heterocyclic ligand decrease in the series: $NH_3 \gg SO_3^= > SO_2 > P(OR)_3$; this can be taken to be the order of increasing π acidity of L.

On this basis, the π acidity of the phosphites, and therefore the stabilization of Ru(II) relative to Ru(III) by back-bonding, increase as follow: $P(O^iPr)_3 < P(OBut)_3 < P(OEt)_3 < P(OMe)_3$. These observations are in agreement with the $E^{o'}$ data and the aquation studies.

Although the *trans*-influence in the phosphite complexes of Ru(II) seems to be due mainly to the pronounced π-acceptor character of the phosphorus atom, the σ bond component may also have some significance. Indeed the equilibrium constants for the isonicotinamide derivatives are higher than those for the corresponding pirazine complexes [5, 9], which may indicate the presence of a synergistic effect between the π and σ bond components in such systems. This subject, as well the '*trans*-effect' in these systems, are currently under investigation in our laboratory and will be reported later.

Acknowledgements

Financial support of this work by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundaçao de Amparo à Pesquida do Estado de São Paulo (FAPESP) is gratefully acknowledged. The author also is indebted to Dr. Frank Quina for revision of the manuscript and to Professors H. Taube and E. Giesbrecht for their aid and encouragement.

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